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STUDIES ON COMPLEXES—XIV[1]

ACCEPTOR PROPERTIES AND STRUCTURE OF 1,4-BISDIAZOCYCLOHEXANETETRAONE, $C_6N_4O_4$

GERALD B. ANSELL, PETER R. HAMMOND and SUSANNE V. HERING
Michelson Laboratories, Naval Weapons Centre, China Lake, California 93555

and

PAOLO CORRADINI*
University of Naples, Italy

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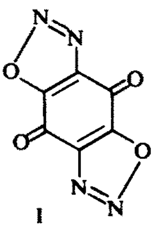
Abstract—Chemical properties of the title compound are described briefly. Coloured solutions with aromatic hydrocarbons, dimethylaniline and polymethoxybenzenes are attributed to 1:1 interactions and equilibrium constants and enthalpies are reported. One, deep-red tetramethoxybenzene complex is isolated. Polarographic reduction in aprotic solvents is irreversible and is compared with the potentials for other acceptors. The compound is a weaker acceptor than trinitrobenzene. An X-ray crystallographic study shows that the molecule is most accurately represented as a bis(diazonium oxide) structure.

EARLIER it was proposed[2] that unsaturated uncharged compounds, contained within the formula $C_wN_xO_yF_z$, comprise a class of covalent materials that are characterised by high electron affinities, namely a class of organic π-electron acceptors. As an example within this class the title compound is studied here.

Henle[3] reported that the diazotization of diaminotetrahydroxybenzene in sulphuric acid gave a compound to which he ascribed the structure benzo-1,4-quinone(2,3-d:5,6-d')bis(1,2,3)oxadiazole (I). A brief description of the same material was given by Mosby and Silva,[4] who prepared it by the action of nitrosyl-sulphuric acid on 2,5-diamino-3,6-dichlorobenzoquinone. Strong IR bands at 4·65 and 6·10 μ were the basis[5] for proposing a bisdiazo-tetraone structure (II).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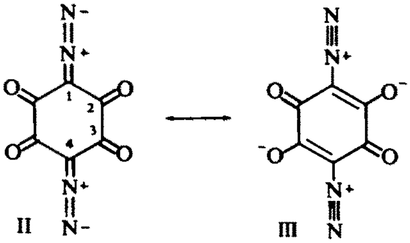
II III

According to the second procedure we obtained 80% yield of heavy (SG 1·73), pale cream crystals, which were prepared analytically pure by water precipitation from nitric acid or by recrystallization from acetonitrile or nitromethane. It is stable in the absence of light, although small heaps exposed to the air or under Nujol darken

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* Visiting Professor at NWC.

irreversibly to brown within three hours on the side nearest to a window. On slow heating, it darkens in the region of 105°C without melting, whereas on rapid heating it deflagrates, impelling the sample tube and leaving a brown residue. It is sparingly soluble in polar solvents—acetonitrile, nitromethane, acetone, ethyl acetate and is practically insoluble in ethanol, ether, alkanes and carbon tetrachloride. The UV spectrum in dichloromethane showed maxima at 317 and 279 mμ, Log ε 4·01 and 4·32 respectively. A low intensity shoulder at 394 mμ, Log ε 2·00 contrasts with the intense transition in this region for *o*-quinonediazide.[6]

ACCEPTOR PROPERTIES

Henle considered dark-red and violet-red adducts with aniline and α-naphthylamine to be products of chemical reactions, although the former decomposed over sulphuric acid in a vacuum. In view of the properties described here, these are seen to be molecular complexes where a donor–acceptor charge-transfer transition is responsible for the colour. The material dissolves in N,N-dimethylaniline or anisole giving red-orange and yellow liquids. Dichloromethane solutions with naphthalene, anthracene, pyrene, perylene, 1,2,4,5-tetramethoxybenzene and dimethylaniline become coloured immediately on mixing—yellow to orange-red—and are stable for several hours. Melts with *sym*-trimethoxybenzene and tetramethoxy-benzene retain their colour—yellow and red—on solidifying. Dark red, near-black needles of a 1:1 complex with the tetramethoxybenzene were prepared from concentrated nitromethane solutions. The continuous variation curve for the anthracene system in nitromethane (Fig. 1) indicates a 1:1 correspondence and it is assumed that the interactions producing the spectra of (Fig. 2) are of this type. On dilution, all absorbances decrease much more rapidly than would be expected if Beer's Law were to apply. From this variation, equilibrium constants were estimated[1] employing six to eight points per run. Inconsistencies for the anthracene interaction in Table 1 are ascribed to experimental error. For the systems with clear absorption maxima, an increase in temperature produces no marked change in band shape, and ΔH values in the range 10–30°C, corrected for solvent expansion are $-1{\cdot}8$ and $-1{\cdot}3$ kcal mole^{-1} for dimethylanilane

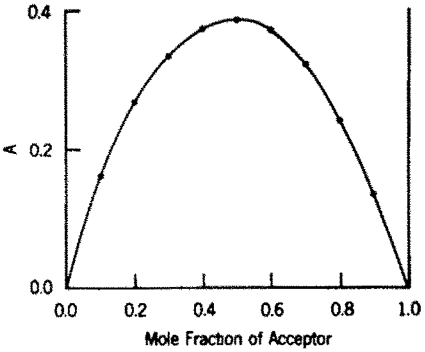

FIG. 1 Continuous variation plots, 5·0 cm cells for 1,4-diazocyclohexanetetraone plus anthracene in nitromethane, A + D = 0·02 M, 450 mμ.

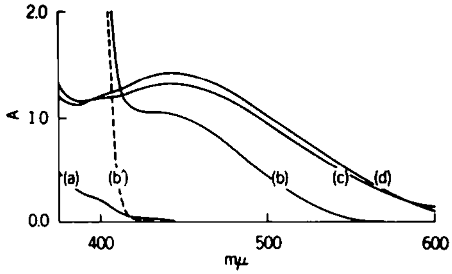

FIG. 2 Spectra of 1,4-diazocyclohexanetetraone systems with donors in dichloromethane. Absorption of cells of DCT 10^{-3} M (a) alone, 2·0 cms, plus (b) anthracene 0·10 M, 5·0 cm, (c) 1,2,4,5-tetramethoxybenzene 0·50 M, 2·0 cm, (d) N,N-dimethylaniline 0·50 M, 2·0 cm (b') anthracene 0·10 M, 2·0 cm alone.

and tetramethoxybenzene respectively. Thus free energy and enthalpy values for the complexes are small in the weakly polar solvent dichloromethane. The maxima are displaced to longer wavelengths for decreasing donor ionization potentials and appear at about 0·25 eV higher energies than for trinitrobenzene systems.

Polarographic reduction measurements on this and other acceptors, some previously studied,[8] are shown in Table 2. Where they overlap, the benzoquinone and chloranil agree with earlier values when account is taken of aqueous—non-aqueous liquid junction potentials. Colours of the reduced solutions are probably those of the anions. An initial pale yellow of chloranil dissolved in dimethyl sulphoxide deepens on reduction. The pale yellow, pale yellow, orange and red colours of solutions of hexacyanobenzene, mellitic trianhydride, tetracyanoethylene, and dicyanodichloroquinone in this solvent are attributed to solvent-acceptor charge-transfer transitions. Fading of the mellitic trianhydride colour within minutes is ascribed to chemical reaction with dimethyl sulphoxide. First wave reversibility was examined for acetonitrile solutions with the aid of single sweep polarography, checking for correspondence of cathodic and anodic waves. On this basis the reductions of benzoquinone, chloranil, hexacyanobenzene and mellitic trianhydride are reversible, with a separation between peaks of about 50 mV. Their potentials have meaning for the comparison

TABLE 1. ASSOCIATION CONSTANTS FOR SOME 1,4-BISDIAZOCYCLOHEXANETETRAONE SYSTEMS IN DICHLOROMETHANE AT 25°

Donor	Wavelength	K (l. mole^{-1})	10^3 ε	10^3 SD
Anthracene	440	0·43	4·8	5
	450	0·30	6·5	4
	460	0·40	4·7	3
Dimethylaniline	450	0·53	3·3	1
	460	0·52	3·3	1
	470	0·53	3·1	1
Tetramethoxybenzene	450	1·03	1·9	6
	460	1·03	1·8	6
	470	1·04	1·7	7

Weighting of points was based on the assumption of a constant variance in absorbance, independent of magnitude. SD is the weighted standard deviation of the ordinate residuals.

of acceptor properties and their order parallels the appearance of charge-transfer maxima with donors. The diazotetraone on the other hand, in the time to perform the reduction–oxidation process (about one second), shows no oxidation peak but merely a shallow wave. The reduction potential, which is more positive than expected on the basis of its absorption maxima, is not an equilibrium one, and the anion must undergo further chemical reaction.

TABLE 2. POLAROGRAPHIC REDUCTION OF SOME ACCEPTORS AT 25° (ELECTROLYTE 0·1N Et_4NClO_4)

Acceptor	Solvent	$E_{\frac{1}{2}}$ vs. SCE		I*		Colour of reduced Species
		E_1	E_2	1	2	
1,4-Benzoquinone	ACN	−0·50	−1·02	2·1	1·4	Yellow
	DMF	−0·45	−1·22	1·7	1·3	Yellow
	DMS	−0·41	−1·22	1·0	0·7	Yellow
Chloranil	ACN	+0·01	−0·71	1·7	2·0	Yellow
	DMF	+0·06	−0·80	1·5	1·3	Yellow
	DMS	+0·07	−0·71	1·3	1·2	Yellow
DCT	ACN	−0·29	−0·84	2·8	1·8	Orange
	DMF	−0·28	−0·85†	1·2	—	Orange-Yellow
	DMS	−0·27	—†	1·0	—	Orange-Pink
Hexacyanobenzene	ACN	−0·12	−0·70	2·3	1·0	Pink
	DMF	−0·07	−0·85	2·0	1·3‡	Orange
	DMS	−0·10	−0·07	1·9	0·8	Orange
Mellitic Trianhydride	ACN	−0·07	−0·33	0·7	0·7	Pink
	DMF	—§	—	—	—	—
	DMS	—§	—	—	—	—

* I is diffusion current constant in μA $mmole^{-1}$ l. $mg.^{-\frac{2}{3}}$ $sec.^{\frac{1}{2}}$ quoted to within 10%.

† Waves indistinct, maxima on further reduction.

‡ Maximum, not suppressed by Triton X-100.

§ No reduction until −1·0 V. Abbreviations: DCT 1,4-bisdiazocyclohexanetetraone, ACN acetonitrile, DMF dimethylformamide, DMS dimethyl sulphoxide.

STRUCTURE

To complete the structure assignment for this and, by implication, other *o*-quinone-diazides, we include the results of an X-ray crystallographic study. The crystals are monochlinic with $a = 8·439$, $b = 7·093$, $c = 6·553$ Å, β 111·7°, d_c 1·75 g. cc^{-1}. The space group is $P2_1/a$ with two molecules per unit cell. Structure determination was based on 418 independent, observed reflections measured by the moving-crystal moving-counter method on a Datex-Automated General Electric single crystal orienter with Ni-filtered Cu-radiation, pulse height selection and a scintillation counter. Two molecules per unit cell imply that each must be centro-symmetric and the two special positions (0, 0, 0), ($\frac{1}{2}$, $\frac{1}{2}$, 0) were chosen as the centres for each. The structure was solved by investigation of a three dimensional Patterson synthesis, consideration of packing requirements and strong reflections, and least-squares structure-factor refinements. At the present stage of the isotropic refinement, the weighted R factor is 0·127 with all atoms having temperature factors between 3·24 to 5·24 $Å^2$. All computations were completed on a Univac 1108 Computer. Bond lengths based on atomic positions at this stage are C(2)—0 (1·23), C(3)—O (1·22), C(1)—C(2) (1·43), C(3)—C(4) (1·41), C(2)—C(3) (1·51), C(1)—N (1·36), and N—N (1·10 Å). These may be compared with known values of C—O (1·23) in ketones, C—C (1·395) in aromatic compounds, C—C (1·541) in paraffins, C—N (1·322) in amides, and the N—N triple bond value (1·131 Å). The molecule is almost planar with all atoms having a deviation less than 0·05 Å from the best least-squares plane through all atoms of the molecule. The observations show clearly that forms such as II, and III in particular, contribute to the structure of the molecule and that I must be rejected.

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